Isotope geochemistry of light hydrocarbons adsorbed in Jurassic shales from the Hils syncline, North-west Germany

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Isotope geochemistry of light hydrocarbons adsorbed in Jurassic shales from the Hils syncline, North-west Germany

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Abstract

The Hils syncline is situated in the south-western corner of the eastern part of the Lower Saxony Basin in which oil has been drilled since 1864. The geochemical data of the reservoired hydrocarbons are well known. In the eastern part of the Lower Saxony Basin, i.e. east of the river Weser, the only source rock of the oil is the Posidonia shale. This sediment, rich in organic matter of kerogen type II, was deposited under uniform anoxic conditions during the Toarcian and reached maturity levels in the oil and gas windows. At the rim of the Hils syncline, which extends to about 40 km in NW-SE direction, the Posidonia shale crops out and shows the same range of maturation as the deeply buried Posidonia shale in the eastern part of the Lower Saxony Basin as a whole.

Five shallow wells with a depth of about 20 m were drilled in the Hils syncline to get core samples from the Posidonia shale and from the shales directly overlying. Gaseous hydrocarbons adsorbed in these samples have been analysed and have been compared with the data set of the reservoired hydrocarbons from the eastern part of the Lower Saxony Basin.

The results of this study show that:

- Gases, adsorbed in the Posidonia shale or neighbouring younger shales of the Hils syncline originated from the Posidonia shale. Their isotopic patterns correspond to the isotopic data of oil-associated reservoir gases from the eastern part of the Lower Saxony Basin. Thus, the Hils syncline can be regarded as a model of the whole eastern part of the Lower Saxony Basin concerning the generation of hydrocarbons.
- The generation of the gaseous hydrocarbons in the shallow cores from the Hils area and of most of the oil-associated gases from the reservoirs of the eastern part of the Lower Saxony Basin must have taken place about 88 million years ago according to the thermal history of the Hils syncline.
- Migration of the light gaseous hydrocarbons from their source rocks to the reservoirs (secondary migration) did not drastically change the isotopic patterns of these gases, i.e. isotopic patterns of migrated gases carry information on source rock properties.
- Considerable amounts of isotopically light methane, ethane, and propane have been observed in many of the gases strongly adsorbed at the cores from the Hils syncline. Isotopically light ethane and propane are unusual.

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1. Structural development, depositional history, and the timing of the petroleum generation in the Hils area

The Hils syncline (Fig. 1) is part of the Leine Hills ("Leinebergland") in southern Lower Saxony (Germany) between the Leine and Weser rivers (Fig. 1, inset map, black square) where the Oxfordian limestones and Albian sandstones form the Ith and Hils mountains (up to 480 m).

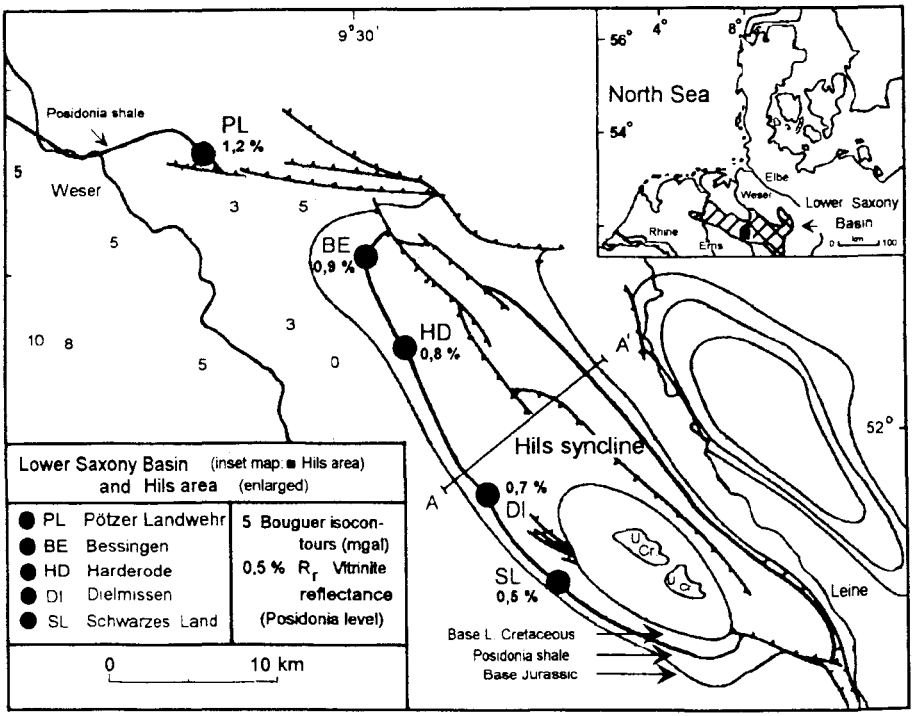

Fig. 1:
Sampling locations in and geology of the Hils syncline, Lower Saxony Basin, North-west Germany

Structurally, it is a complex graben in graben structure situated in the south-eastern central part of the Lower Saxony Basin which is a highly complex mesozoic (Late Jurassic to Early Cretaceous) graben basin. It inverted, i.e. compressed and elevated, in Santonian (Late Cretaceous) time. The Hils structure is filled with sediments of Late Jurassic age. In its centre Tertiary and remnants of Late Cretaceous sediments are still preserved. This central filling is surrounded by argillaceous Early and Middle Jurassic sediments outcropping at the surface (Fig. 2).

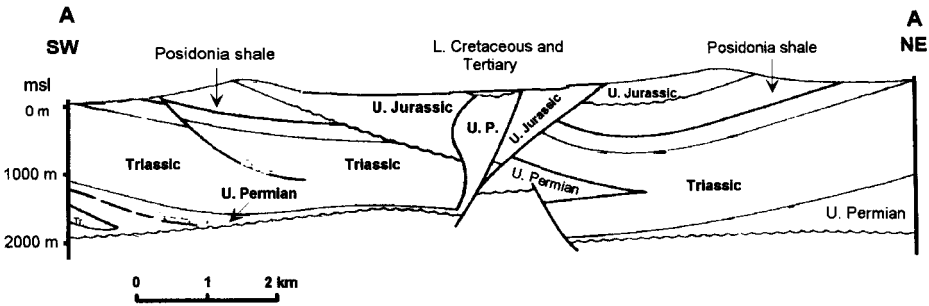

Fig. 2:
Geologic cross section through the Hils syncline (cf. Fig. 1)

In Early Jurassic times, precisely during the Early Toarcian, the Lower Saxony Basin and with it the Hils graben structure did not yet exist. The entire North Sea Basin including the North German Basin, southern Britain, northern France, and even southern Germany was covered by a shallow, anoxic sea in which the Posidonia shale, in general only 25 m thick, was deposited (Fig. 3). This layer of marine black shale is the most prominent, if not the only petroleum source rock in many hydrocarbon-bearing basins as the Paris Basin, the southern English Basins and the Lower Saxony Basin. In southern Germany it became famous due to the findings of numerous well preserved vertebrates at Holzmaden.

The subsidence of the North European Mesozoic Basin, at a later date containing the Lower Saxony Basin, continued during the Middle Jurassic. In Late Jurassic (Tithonian) times, the generally WNW-ESE striking Lower Saxony Basin and with it the Hils structure separated from the larger North European Basin and transformed into a rapidly subsiding complex graben. The bordering faults were synsedimentarily active, especially during the Tithonian. At the end of the Turonian when this continuous subsidence ceased, the Posidonia shale in the centre of the Hils graben reached a maximum depth of 2000 m below sea level, sufficient enough to cause an average maturity (vitrinite reflectance) of R_r = 0.4 % to 0.5 % and to start the generation of oil and gas from the organic matter of the shale. Traces of oil and asphalt are ubiquous in and around the Hils structure.

The inversion of the Lower Saxony Basin and with it that of the Hils structure started in Coniacian times (88 million years b.p.). The former graben features became uplifted, the graben filling was overthrusted along the former faults onto the former graben shoulders. The inversion lasted about 5 million years to the end of the Santonian. Later the individual inversion structures became deeply eroded below the Campanian unconformity and again before the Late Paleocene transgression. The former erosion surface can be recognized in the peneplain which is partly preserved in the present day morphology. Detailed information on the structural evolution of the Leine hills has been published by Jordan & Kockel, 1991.

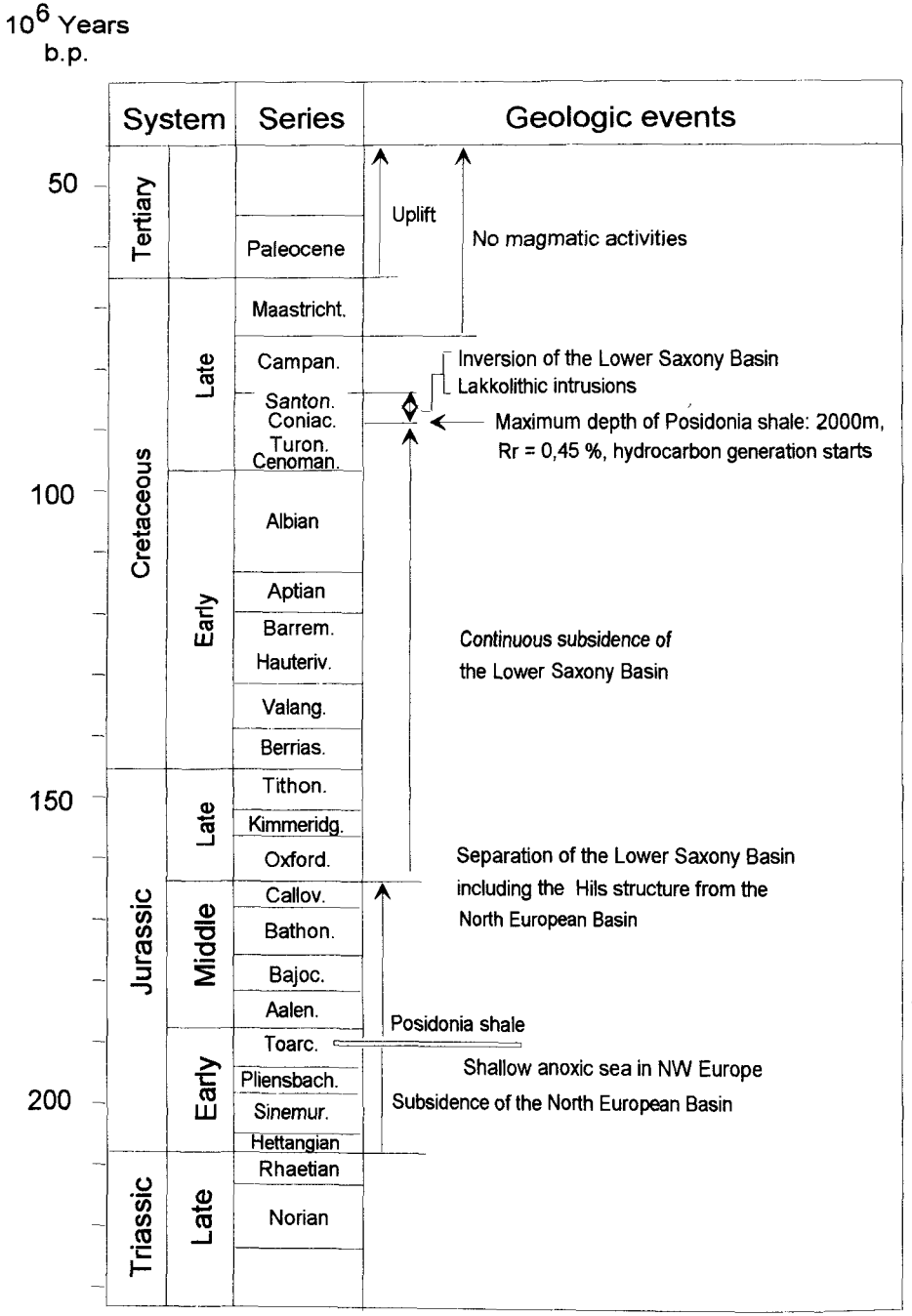

Fig. 3:
Main geologic events

Probably contemporaneously with the inversion, at least later than Late Aptian (Eckhardt, 1991), the centre of the inverted Lower Saxony Basin was intruded by large lakkolithic bodies of unknown petrology, well recognizable by magnetic, gravity and coalification anomalies (see Fig. 1). The largest of these bodies is the Bramsche massif in the western part of the Basin, another one the Vlotho massif, the thermal aureole of which prolongated eastwards below the north-western tip of the Hils structure. The average maturity of $R_r = 0.45\%$ encountered in the south-eastern part of the Hils structure is due to mere subsidence before the inversion in Coniacian-Santonian times which lifted the source rock into very shallow depths. The elevated maturity values in the north-western part of the area, however, result from an additional heat source connected with the eastern extensions of the Vlotho intrusive body. This intrusive influenced its sedimentary cover for a short time of about 5 million years. It is unlikely that the Late Cretaceous and the Tertiary structural evolution of the area had noticeable effects on the maturity of the source rock as no young magmatic activity is known, and since the beginning of the Tertiary (65 million years b.p.) uplift overcompensated young subsidence. The thermal and depositional history of the Hils syncline summarized in Fig. 3 leads to the conclusion that the hydrocarbon generation in the Hils area had ceased already with the beginning of the Campanian 83 million years b.p.

2.1 Sampling and sampling area

The Posidonia shale of the Hils area has been the target of recent investigations:

Wintershall AG, a German Oil Company, has drilled and cored wells down to a depth of up to two hundred meters. The results are unpublished.

Leythaeuser and co-workers have investigated the Posidonia shale of the Hils syncline with special regard to the phenomena of the primary migration of the $C_{15}+$ fraction (Leythaeuser et al. 1988, Littke et al. 1988, Mann 1987). Their wells reached a maximum depth of about 80 meters.

The 20 m-wells of the Federal Institute for Geosciences and Natural Resources in Hannover, drilled in December 1990, are marked in Figure 1 by full circles (this paper). At each sampling site, a profile of shallow boreholes was drilled from a location next to the outcrop of the Posidonia shale in direction to the centre of the syncline. The sampling strategy is presented in Figure 4 where the site "Schwarzes Land" (SL) is taken as an example. The drillhole A is situated next to the outcrop. The wells B to E are shifted towards the centre of the syncline.

Generally, the target of the drilling were the Posidonia shale or younger shales. Measurements showed that the maturity of the neighbouring but stratigraphically different shales in a well was identical. The mean total amount of organic carbon (TOC) generally decreased from up to 4.7 % in the Posidonia shale to approximately 0.5 % in the younger shales (Tab. 1, appendix). Vitrinite reflectance and Rock Eval measurements of the organic matter of the core material from the shallow series of the shallow drillholes Schwarzes Land (SL), Dielmissen (DI), Harderode (HD), Bessingen (BE) and

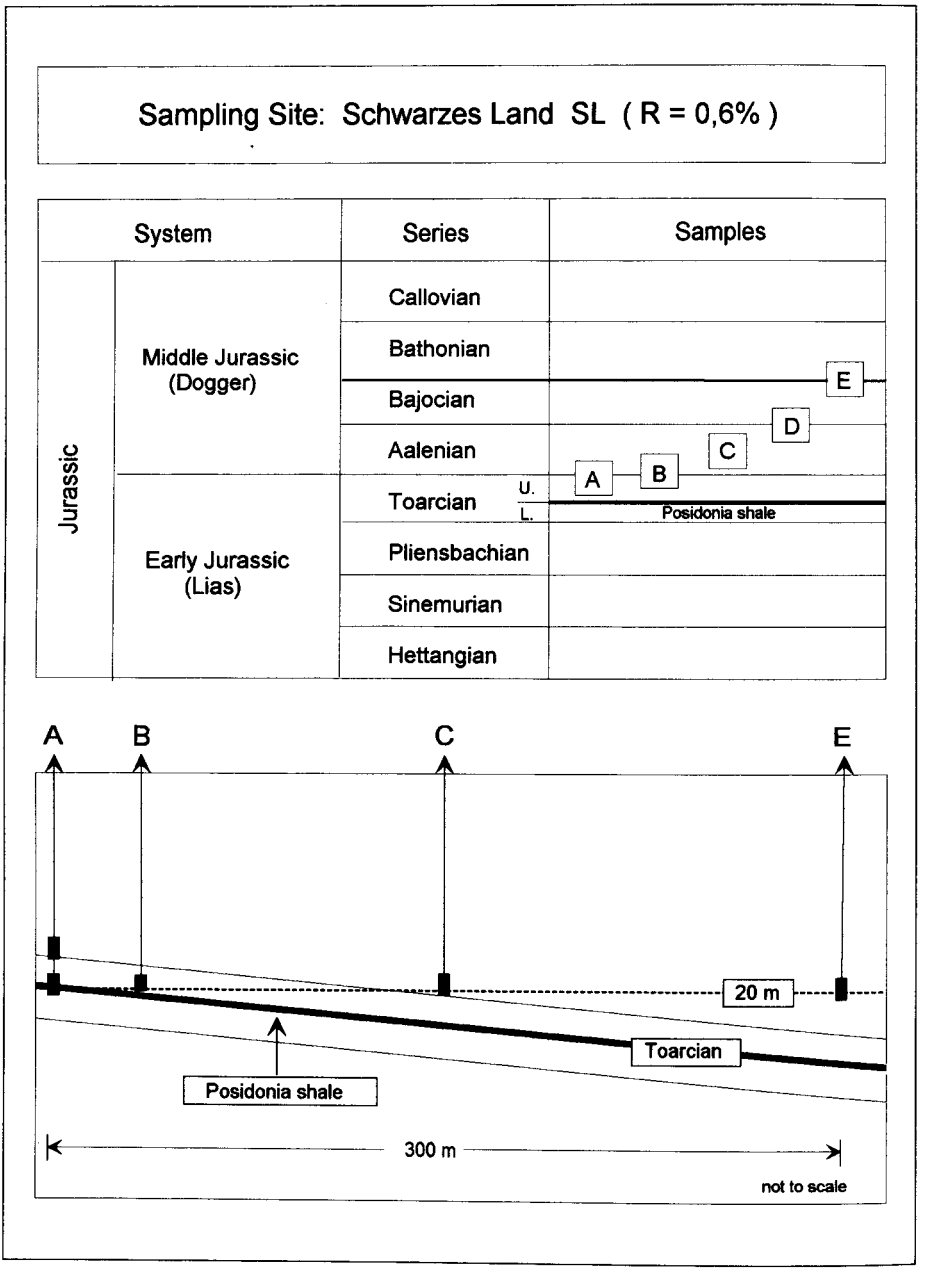

Fig. 4:
Location of the shallow wells and stratigraphic situation at the sampling site "Schwarzes Land"

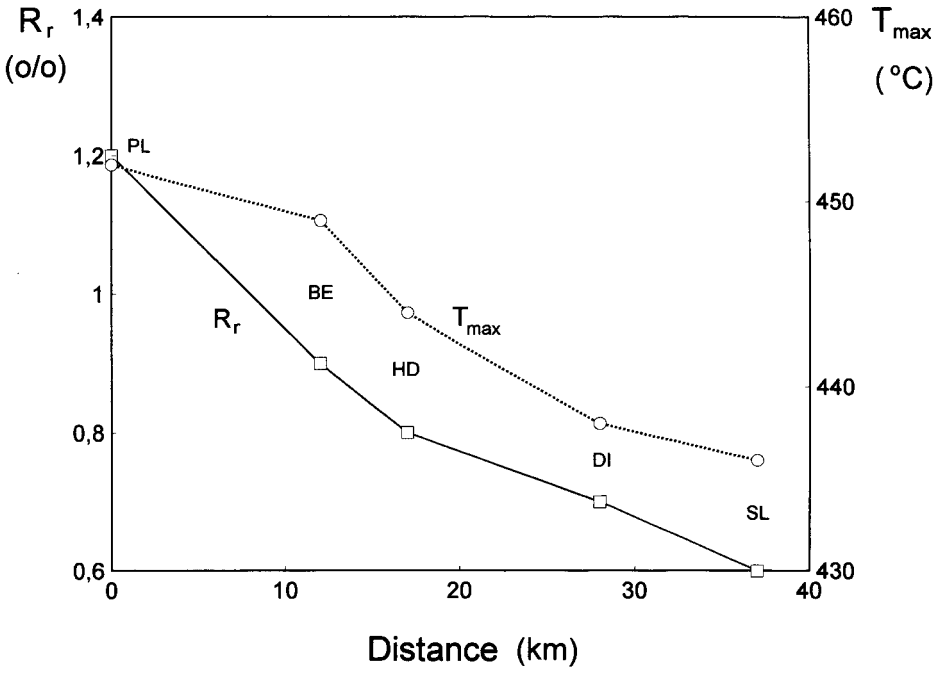

Fig. 5:
Regional changes of the random vitrinite reflectance R_r and T_{max} on a NW-SE profile through the sampling sites

Pötzer Landwehr (PL) confirm the known patterns: Low maturities, characteristic of the beginning of oil generation in the SE part, relatively high maturity values at the NW corner of the Hils syncline (Fig. 5).

These maturity data are – within the limits of experimental errors – in accordance with the results published by Rullkötter and co-workers (1988).

3. Experimental approach and results

The core samples were stored in liquid nitrogen immediately after drilling until the degassing in the laboratory. The laboratory procedure from the degassing of the cores over the separation and oxidation of the degassed hydrocarbons to the isotope mass spectrometry is described by Faber & Stahl (1983) and Dumke et al. (1989). The results of the organic geochemical and isotopic investigations are listed in Table 2 (appendix).

4. Discussion of the results

4.1 Geochemical patterns of gas properties at selected sampling sites

The geochemical gas properties of hydrocarbons mainly depend on the type and maturity of their source rocks. The analytical results of the adsorbed gases from the sites SL, HD, and PL have been selected for detailed discussion. These samples represent a broad range of source rock maturities ($0.6\% < R_r < 1.2\%$). The gas data from the sampling sites Bessingen (BE) and Dielmissen (DI) are included in Table 2. They fit into the regional trends of the other three sampling sites. The gas yields of the samples from the site DI-D are small so that background contaminations are quite probable.

4.11 Schwarzes Land (SL)

The stratigraphic position of the samples at the drillhole SL-A reach from the base of the Upper Toarcian to the lower Bathonian (Fig. 4). The vitrinite reflectance of the Posidonia shale and of the adjacent younger shales is $R_r = 0.62\%$ at this site.

The variation of the yields of the adsorbed hydrocarbons from ethane, butane, and hexane with depth is shown in Figure 6.

The yields of the samples SLA-12 and SLA-10 next to the underlying Posidonia shale (Upper Toarcian, Tab. 2) are high and decrease in the adjacent younger shales. They are at a minimum in the overlying Middle Jurassic. The yields of the saturated hydrocarbons C_1 to C_6, however, are high at any depth, even in the uppermost sample of site A in comparison with other data of surface exploration surveys (e.g. Faber & Stahl, 1984).

The existence of relatively large quantities of light hydrocarbons adsorbed at the Hils cores generates a principal problem. Even if one accepts only diffusion as the slowest physical process of migration, the light hydrocarbons should have been escaped more or less completely into the atmosphere during the past time of more than 80 million years (cf. Leythaeuser et al. 1982). This means that other processes – slower than diffusion – are active in this "inactive" source rock. Probably ad- or absorption of hydrocarbons on the clay surfaces plays a stronger role in gas preservation than commonly accepted.

A present-day generation of these hydrocarbons is very unlikely because of the more or less continuous uplift of the basin probably since the Late Cretaceous, surely since the beginning of the Tertiary. The maturity of $R_r = 0.62\%$ has been reached 88 million years ago and has not been changed in the following times. Therefore, the bulk of gaseous hydrocarbons, strongly adsorbed at the shales, must either have been generated in-situ about 88 million years ago or should have migrated to the sites where we find the gases nowadays. Also both possibilities could have contributed to the present depth variations of the gas yields. Figure 7 shows decreasing mean concentrations of organic matter and decreasing yields of the methane adsorbed in the core samples SL-A to SL-E on a 300 m profile which extends from the outcrop of the Posidonia shale in direction to the centre of the syncline.

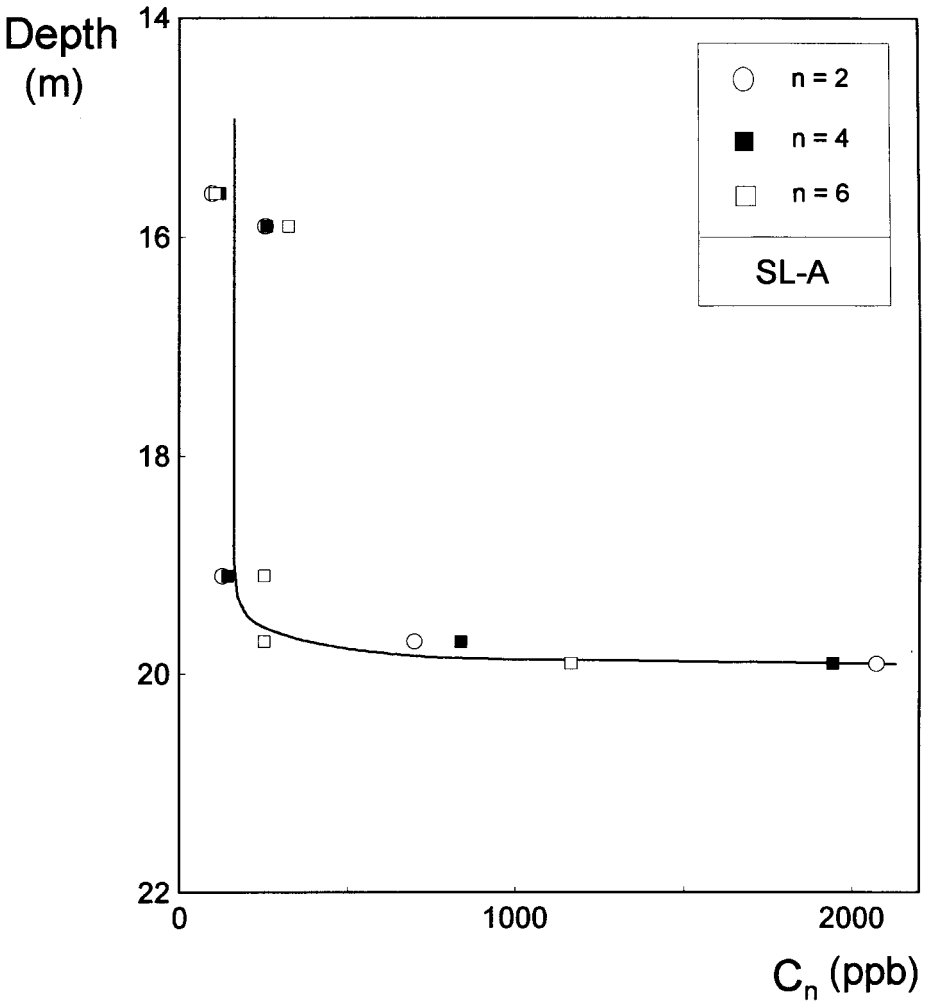

Fig. 6:
Variations of hydrocarbon gas yields with depth at the shallow well SL-A

The samples, generally taken at a depth of about 20 m, represent shales from the Upper Toarcian to the Lower Bathonian, i.e. shales containing different types of organic matter (Littke et al., 1988). The positive correlation (Fig. 7) between the total amount of organic carbon (TOC) and the yields of the adsorbed methane (C_1) could indicate an in-situ generation of the methane from the organic matter of the stratigraphically different cores. The $\delta^{13}C_1$ values of the adsorbed methane, however, are rather uniform and scatter only between −44‰ and −41‰ (Fig. 7). They point to an origin of the methane from a source rock of kerogen type II and to a maturity within the

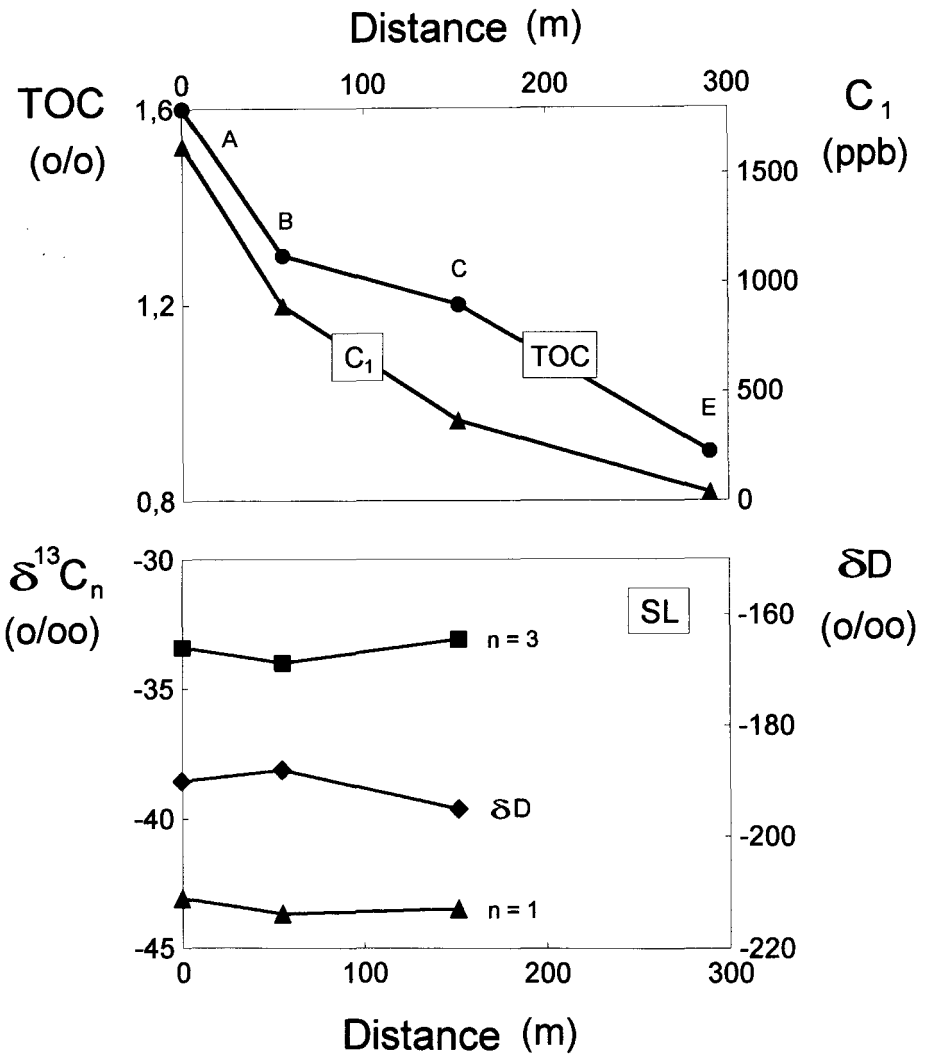

Fig. 7:
Regional variations of geochemical data on a profile through the shallow wells SL-A to SL-E. The isotope ratios at SL-E are omitted because they are probably affected by background gas from the laboratory lines due to the small gas yields.

oil window (Faber, 1987). The uniformity of the isotope ratios of the gases, adsorbed at stratigraphically different shales, containing different types of organic matter, is an argument that the origin of the gases is the Posidonia shale and that the generally decreasing gas yields with decreasing sampling depth or with stratigraphically younger samples has been caused by migration.

The maturity range derived by the isotope ratios of the adsorbed methane, ethane, and propane at the sampling site SL-A is slightly too high in comparison with the vitrinite reflectance $R_r = 0.62\%$, measured directly on the organic matter of the SL-A samples. This discrepancy can be explained by the differences of the type of organic matter in the Posidonia shale and in the overlying younger sediments. Littke and co-workers (1988) reported that "... in contrast to the very high initial organic matter content of the Posidonia shale (av. = 10.7% at Wenzen), the adjacent shales contain little organic matter of type III kerogen quality". The small portion of organic matter of kerogen type III must have generated small amounts of ^{13}C enriched hydrocarbon gases which mixed with the relatively large quantities of gaseous hydrocarbons from the Posidonia shale, the source dominating the geochemical patterns of the adsorbed gases. This interpretation explains the small fluctuations of the isotopic data with depth and also the slight discrepancy between the vitrinite reflectance measurements and the isotopically derived maturities. It shows that the bulk of the gaseous hydrocarbons originated from an organic matter of kerogen type II and most probably migrated from the Posidonia shale to the overlying rock column.

The very small amounts of hydrocarbons gained from the sample site E (methane: 37 ppb) are ^{12}C-depleted ($\delta^{13}C_1 = -34.0‰$) in comparison with the samples from the other sites. Our laboratory experienced that the isotope ratios measured on quantities of methane smaller than 50 ppb are shifted in favour of the heavier carbon isotope during the laboratory procedure. Such a shift has been observed for samples with methane close to background concentrations (Faber & Stahl, 1984). It is likely that the methane adsorbed at the samples from site E is isotopically contaminated by the background gas of the combustion line.

The results of the analyses of gases desorbed from shallow cores of the site Schwarzes Land (SL) show that

- considerable amounts of the methane to hexane hydrocarbons nowadays are still adsorbed at the shales, although the generation of these hydrocarbon gases must have ceased about 80 million years ago,
- the origin of the bulk of the adsorbed gases is a kerogen of type II in a maturity range equal or at least very similar to that of the underlying Posidonia shale. Therefore, it is very probable that most of the gaseous hydrocarbons has been generated by the Posidonia shale,
- small amounts of ^{13}C enriched, probably autochthonous gaseous hydrocarbons must have been admixed to the Posidonia shale gases during upward migration.

4.12 Harderode (HD)

The stratigraphic position of the drillholes HD-A to HD-E at the sampling site Harderode is the Upper Toarcian/Lower Aalenian boundary. The vitrinite reflectance of the Posidonia shale and of the adjacent younger shales is $R_r = 0.79\%$.

The averaged carbon isotope data (Fig. 8) demonstrate that considerable quantities of the methane at the sampling location HD is of bacterial origin ($\delta^{13}C_1 < -50‰$). On the other hand, the high yields of ethane and propane (Tab. 2, Fig. 9) point to

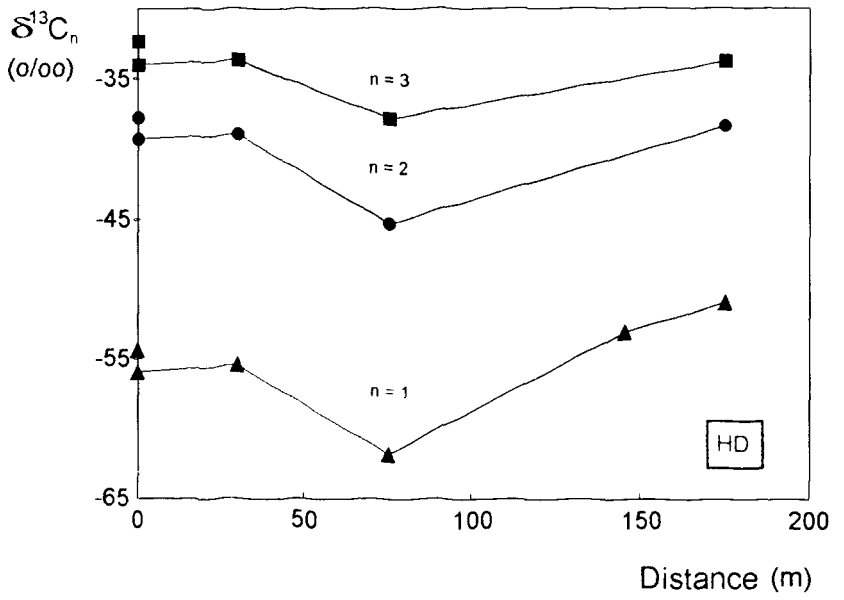

Fig. 8:
Variations of the mean carbon isotope composition of methane, ethane, and propane on a profile at the sampling site Harderode

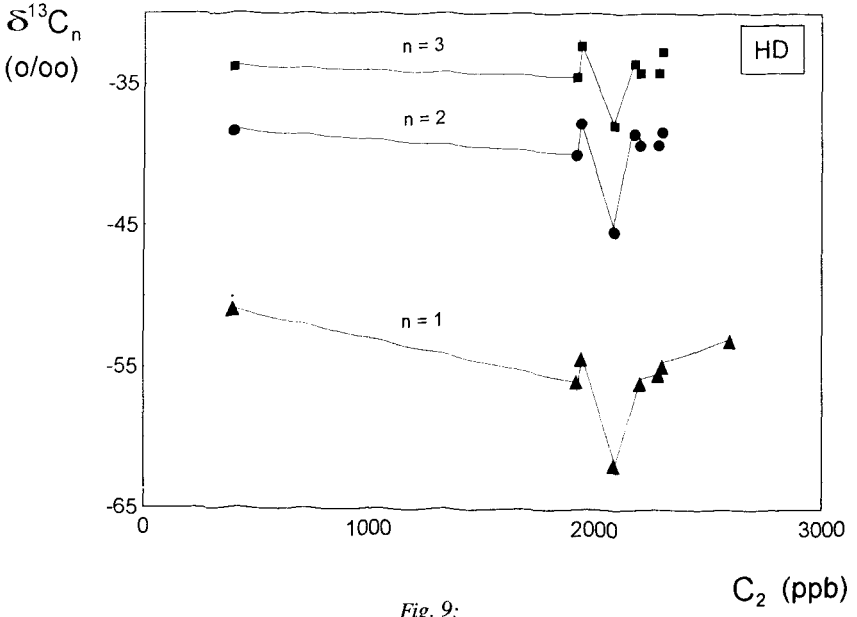

Fig. 9:
The carbon isotope composition of methane, ethane, and propane in relation to the ethane content of gases adsorbed at cores at the sampling site Harderode.

a contribution of thermal gas from a kerogen of type II. The carbon isotopes of the ethane and propane, however, follow the trend of the methane (Figs. 8, 9) indicating that also these higher homologues are likely mixtures of conventional thermal hydrocarbons and of an unusual type of ethane and propane, which is isotopically light. If the isotopically unusual ethane and propane gases had not been generated by bacteria, the origin of the isotopically light portion of methane could also be in part of an unknown origin.

4.13 Pötzer Landwehr (PL)

The stratigraphic position of the samples drilled PL-A to E at the drilling sites of Pötzer Landwehr is the Posidonia shale. Only the sample PL-F is stratigraphically situated at the Toarcian/Aalenian boundary.

The classification based on biostratigraphical investigations is likely to be correct, although the high maturity of R_r = 1.2% has eliminated the "Tasmanales", typical of the Posidonia shale. Other properties of the samples, as stratification, colour, smell and especially the relatively high content of organic matter strongly suggests that the samples PL-A to PL-E stem from the Posidonia shale. The variation of the carbon isotopes of the methane, adsorbed at the shale samples of Pötzer Landwehr, covers a range of approximately 15‰.

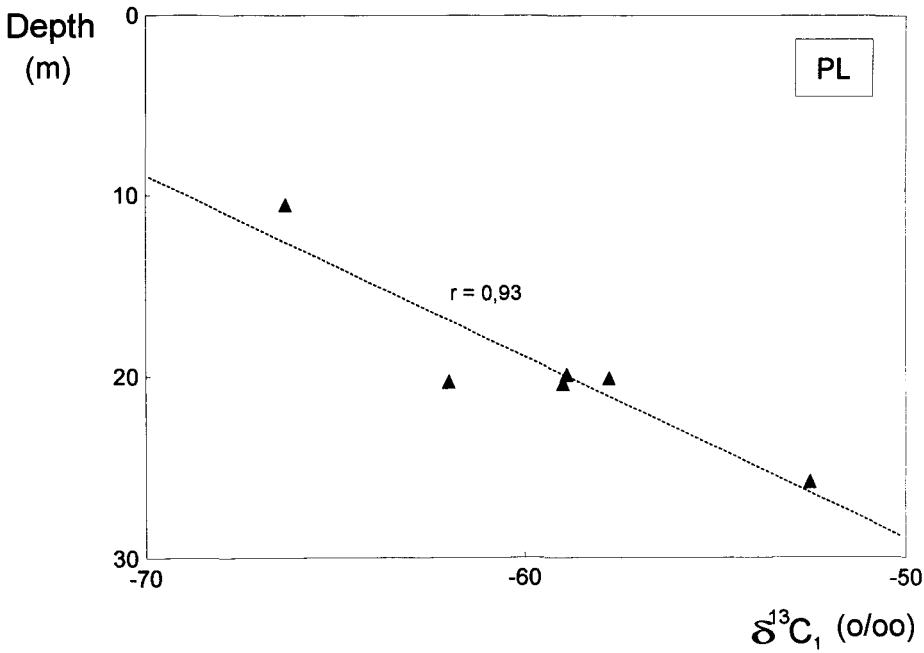

Fig. 10:
Variation of the carbon isotopic composition of the methane with depth at the sampling site Pötzer Landwehr

The carbon isotope ratios of the methane from the cores of Pötzer Landwehr change with decreasing sampling depth in favour of the light isotope indicating increasing contributions of bacterial methane (Fig. 10).

Similar to the situation at Harderode the correlation between the $\delta^{13}C$ values of the methane on the one hand and the $\delta^{13}C$ values of the ethane and propane on the other hand are indications that isotopically light ethane and propane show up with the adsorbed gases.

4.2 Isotopically light methane, ethane, and propane strongly adsorbed in shales

The existence of bacterial methane strongly adsorbed in shale samples from the Hils area is shown in Figures 8 to 10. Although it is very common that bacterial methane shows up as "free gas", for example as head space gas, it is unusual to find large amounts of bacterial methane strongly adsorbed at shales. It is even more unusual to detect strongly adsorbed, isotopically light ethane and propane. These strange gases occur in that part of the Hils syncline, where the thermal impact of the intrusive of Vlotho has rapidly increased the maturity of the organic matter (PL, BE, HD). The contribution of bacterial methane to the adsorbed gas increases in direction to the masssif of Vlotho (Fig. 11).

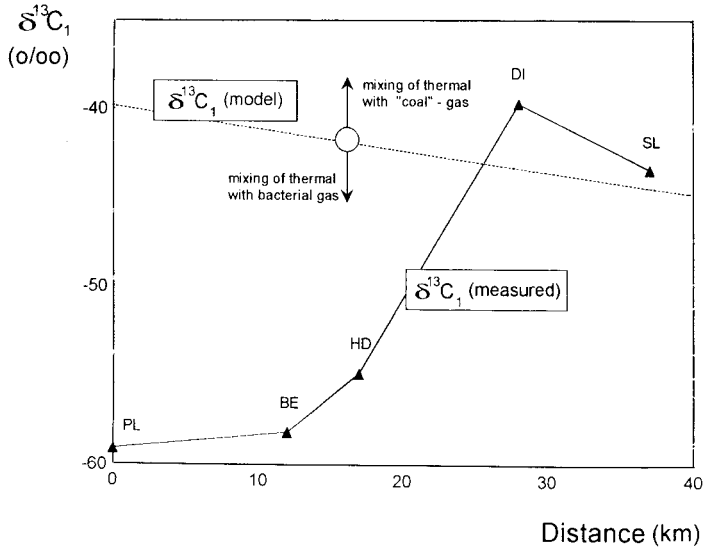

Fig. 11:
Comparison of the measured isotopic composition of the adsorbed methane with the calculated δ-values. The calculation is based on the maturity of the Posidonia shale at the sampling sites according to the model of Faber (1987). The sampling sites are projected onto a NW-SE profile through the Hils syncline.

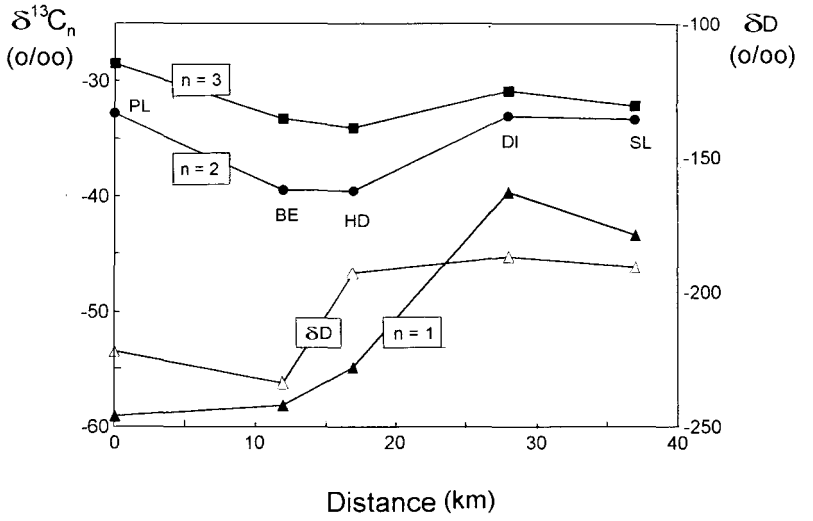

Fig. 12:
The carbon isotopic composition of the methane, ethane, and propane and the deuterium content of the methane strongly adsorbed at shale samples

Fig. 11 shows that small amounts of ^{13}C enriched gas (kerogen III) could be a constituent of the adsorbed gases from the locations Schwarzes Land and Dielmissen, although the mean isotopic composition is clearly outside the limits of experimental errors only at the sampling site Dielmissen. But at this site background gases could have contributed to the isotope shift in favour of the heavier carbon isotope (cf. 4.1).

The deuterium concentration of the methane approximately follows the trend of the ^{13}C isotopes (Fig. 12). The carbon isotopic composition of the ethane and propane is most ^{12}C enriched at Bessingen and Harderode and approaches the model data (Faber 1987) at Pötzer Landwehr and Schwarzes Land.

To date, the origin of the unusual isotopically light hydrocarbons is not clear. Some of the possible explanations are:

- The isotopically light ethane and propane gases partly could be of bacterial origin comparable to the isotopically light methane. In this case the thermal event related to the massif of Vlotho should have expelled the formerly generated thermal gases strongly adsorbed at the adsorption sites of the shales at a higher rate than the thermal generation rate of gases from the indigineous organic matter under the elevated heat flow of the intrusive. Paleo-bacterial gases, still present in the reducing environment of the Posidonia shale, could penetrate to the partly empty adsorption sites, becoming strongly adsorbed. Due to the fact that this thermal event of Vlotho

and related to it the thermal gas generation lasted only for approximately 5 million years, there has not been time enough to exchange or remove all the bacterial gases at the adsorption sites of the shale by the newly forming thermal hydrocarbons.

- The isotopically light ethane and propane could stem from the fluid system related to the uplit of the massif of Vlotho.
- The isotopically light ethane and propane could have been generated thermally under the special conditions of the heat impact of the massif of Vlotho. A pyrolysis of the degassed shale samples should yield isotopically light ethane and propane gases in this case.

The carbon isotopic compositions of the ethane and propane of the pyrolysis (Maaß 1991) on the one hand and of the adsorbed gases on the other hand are very similar. Both populations scatter around the 45 degree line in Fig. 13. The same holds true for the isotope data of the methane from Schwarzes Land and Dielmissen. These indications favour a thermal generation of these hydrocarbons from the Posidonia shale.

The carbon isotopes of the methane from the pyrolysis of the shale samples from Harderode, Besssingen and Pötzer Landwehr are approximately in line with the isotopic composition derived by the model of Faber (1987) in contrast to the corresponding adsorbed methane gases which are isotopically too light. This indicates that a portion of the methane, adsorbed at these cores, is not a thermal gas, but could probably be of

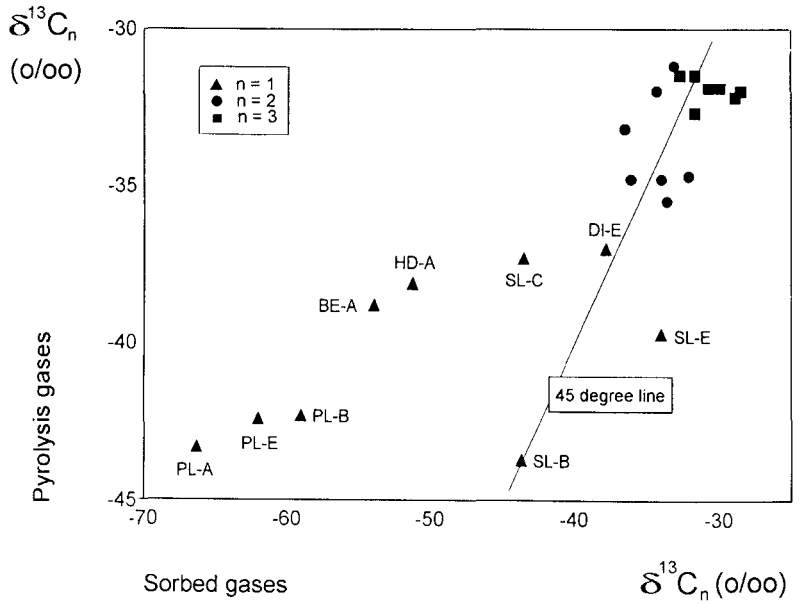

Fig. 13:
Comparison of the carbon isotopic composition of gases, strongly adsorbed at the shales and pyrolysis gases from these shales

bacterial origin. The origin of the isotopically light ethane and propane – possibly related to the thermal event caused by the massif of Vlotho – is not yet understood.

4.3 Comparison of the geochemical data of gases from petroleum reservoirs of the eastern part of the Lower Saxony Basin with the data of the gases adsorbed in shallow cores from the Hils Syncline

The source rock situation concerning maturity and type of organic matter is the same in both the whole eastern part of the Lower Saxony Basin (Binot et al., in print) and in the Hils syncline. Structural, source rock and hydrocarbon data for the Lower Saxony Basin are well known (Kockel et al., 1991; Wehner et al., 1988). Data of hydrocarbon gases from the oil reservoirs of the eastern part of the Lower Saxony Basin have been presented by Gerling and co-workers (1989, 1991).

The carbon isotopes of the methane and the ethane of the desorption gases from cores of the Hils syncline are compared with the corresponding isotope data of reservoir gases from the eastern part of the Lower Saxony Basin in Figure 14.

The isotopic pattern of a considerable part of the adsorbed methane and ethane desorption gases from cores of the Hils syncline are in the isotopic range of the reservoir gases. Another set of adsorbed gas data, however, is situated outside the data box of the 110 reservoir gases indicating the existence of different types of adsorbed gases. Obviously, considerable mixing of different gas types occur.

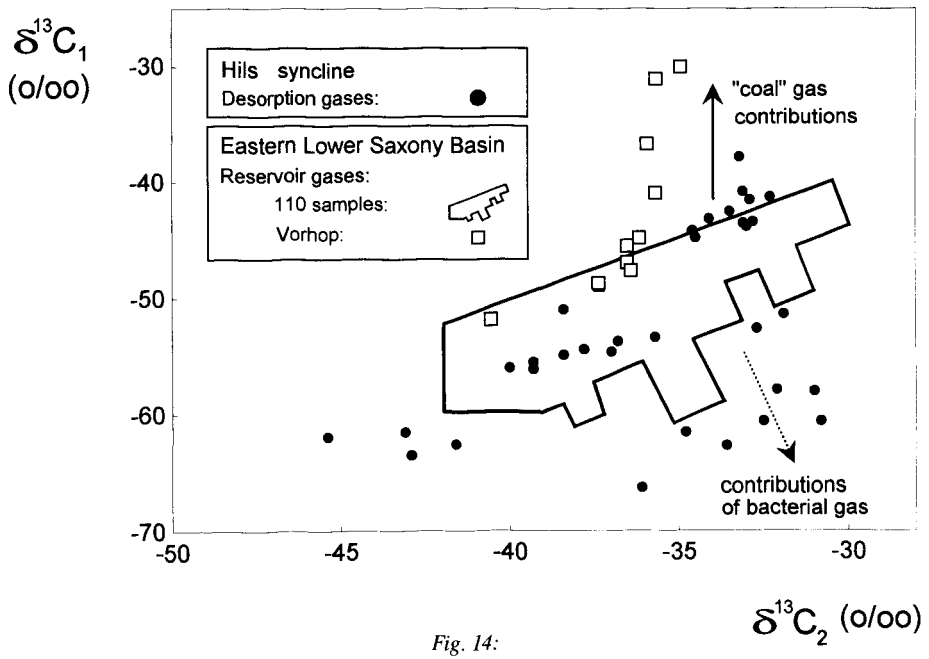

Fig. 14:
Comparison of the carbon isotope compositions of methane and ethane gases, strongly adsorbed at the cores from the Hils syncline and of reservoir gases from the eastern part of the Lower Saxony Basin

Admixing of bacterial methane to reservoir gases has already been observed by Faber (1987). The shape of the data box of the reservoir gases (Fig. 14) also points to contributions of bacterial gas.

Several samples of adsorbed gases show the opposite tendency: they are ^{13}C enriched. The same trend has been reported by Gerling and co-workers (in preparation) in their paper on the reservoir gases of the Vorhop field, where "coal" gases from the Upper Carboniferous migrated into the oilfield Vorhop. Vorhop is situated in the eastern part of the Lower Saxony Basin and mainly sourced from the Posidonia shale.

The complications, caused by mixing, might not occur if methane is excluded from the comparison of reservoir and adsorbed gases.

The good accordance between the isotopic patterns of reservoir and adsorbed gases (Fig. 15) shows that the bulk of the ethane and propane gases, adsorbed at the Hils cores, originated from a source rock very similar or identical to the source of the reservoir gases of the eastern part of the Lower Saxony Basin, i.e. the Posidonia shale. Moreover, this good accordance is a strong argument that migration, which definitely affected the reservoir gases on their preferably vertical and short range migration path from their source to their reservoirs, did not drastically change the isotope ratios of the migrating hydrocarbons.

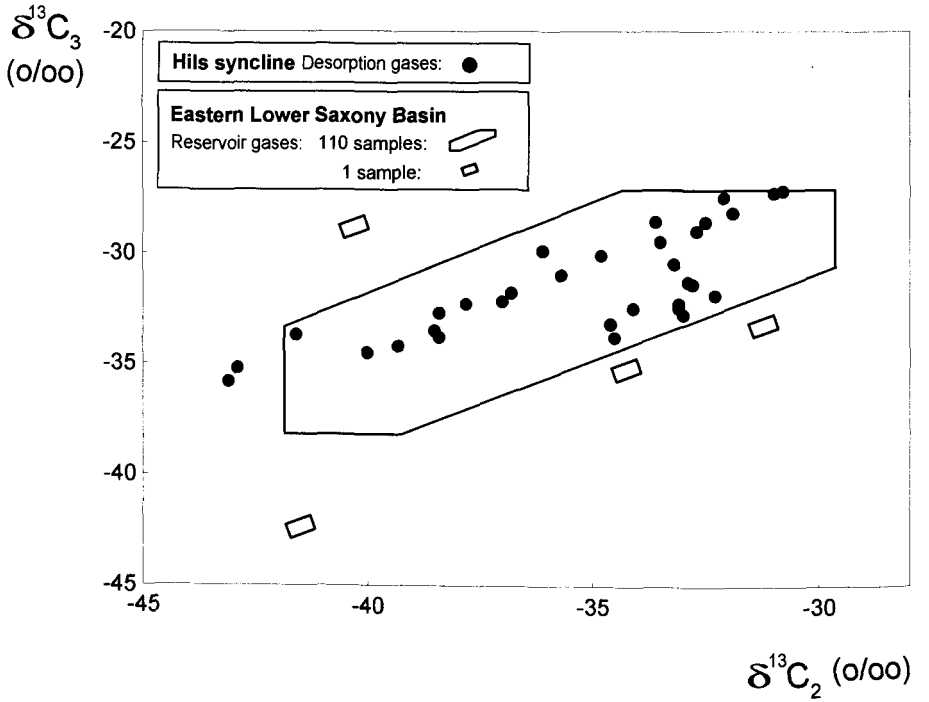

Fig. 15:
Comparison of the carbon isotope compositions of ethane and propane gases, strongly adsorbed at the cores from the Hils syncline and of reservoir gases from the eastern part of the Lower Saxony Basin

5. Conclusions and summary

Investigations of the hydrocarbons, strongly adsorbed at shallow cores from the Hils syncline are summarized as follows:

- The adsorbed gases of the analysed cores have been generated predominantly by the Posidonia shale. They migrated to their present adsorption sites. This migration must have ceased more than 80 million years ago when according to the basin history the subsidence stopped and an uplift took place in the following time.
- The existence of relatively large quantities of hydrocarbon gases adsorbed at the Hils cores is not understood. They should have been lost by diffusion to the atmosphere during the past time of more than 80 million years. Probably ad- or absorption of hydrocarbons on the clay surfaces of this source rock plays a strong role in gas preservation.
- The carbon isotopes of the ethane and propane of oil-associated gases from the Lower Saxony Basin and of the adsorbed gases from the shallow cores of the Hils syncline are in good accordance. This holds true for the methane gases adsorbed from those sampling sites which are not thermally influenced by the massif of Vlotho and demonstrates that the isotopic patterns of many gases adsorbed in Hils cores correspond to the isotopic data of oil-associated reservoir gases and originated from the same type of source rock at the same maturity levels.
- Admixing of bacterial and "coal" methane has been observed in both sets of data.
- Isotopically light methane, ethane, and propane are components of the hydrocarbons strongly adsorbed at the sediments of the Hils area. They could be a minor constituent of the reservoir gases of the Lower Saxony Basin.
- Secondary migration, i.e. the migration of the gases from their source rocks to their reservoirs has not, at least not drastically, changed the isotopic patterns of these gases: isotope data of migrated light hydrocarbons give reliable information on source rock properties.

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Tab. 1: Geochemical data, averaged over the samples from the wells SL, DI, HD, BE and PL. Column 1 shows the distances among the wells projected onto a NW-SE profile. The samples SL-E and DI-D have been omitted due to small gas yields.

Site	Distance (km)	TOC (%)	Rr (%)	T_{max} (°C)	C_1 (ppb)	C_2 (ppb)	C_3 (ppb)	iC_4 (ppb)	nC_4 (ppb)	C_4 (ppb)	C_5 (ppb)	C_6 (ppb)	C_2= (ppb)	$\delta^{13}C_1$ (o/oo)	δDC_1 (o/oo)	$\delta^{13}C_2$ (o/oo)	$\delta^{13}C_3$ (o/oo)
SL	37	1.9	0.6	436	1037	373	334	134	261	395	550	618	2	−43.4	−190.7	−33.4	−32.2
DI	28	0.5	0.7	438	487	143	70	41	39	80	91	68	27	−39.7	−187	−33.1	−30.9
HD	17	1.1	0.8	444	3585	1827	1179	350	616	967	955	2853	5	−54.9	−193	−39.6	−34.1
BE	12	1.3	0.9	449	7844	3617	1164	395	711	1106	798	774	4	−58.2	−233.7	−39.5	−33.3
PL	0	4.7	1.2	452	20428	6712	2629	645	1091	1736	1131	1314	19	−59.1	−221.8	−32.8	−28.5

C_1: methane
C_2: ethane
C_3: propane
iC_4: isobutane
nC_4: normal butane
C_5: pentane
C_6: hexane
C_2=: ethane

TOC: total organic carbon
R_r: random vitrinite reflectance
T_{max}: max. hydrocarbon generation during pyrolysis

Tab. 2: Analytical results

Sample	Biostrati-graphy	C_1 (ppb)	C_2 (ppb)	C_3 (ppb)	iC_4 (ppb)	nC_4 (ppb)	C_5 (ppb)	C_6 (ppb)	$\delta^{13}C_1$ (o/oo)	δDC_1 (o/oo)	$\delta^{13}C_2$ (o/oo)	$\delta^{13}C_3$ (o/oo)
SL-A02		432	119	84	43	54	183	106	−43,4	−160	−32,8	−31,4
SL-A03		982	259	198	108	147	357	323	−43,5	−183	−33,1	−32,3
SL-A04		525	144	102	39	90	137	254	−41,3	−174	−32,3	−31,9
SL-A10	2	2590	838	627	256	444	826	253	−43,2	−219	−34,1	−32,5
SL-A12	2	3621	1941	2052	587	1484	1931	1165	−44,2	−212	−34,6	−33,2
SL-B06	4	993	237	185	124	162	327	502	−44,8	−206	−34,5	−33,8
SL-B08		795	215	176	158	219	530	621	−42,5	−169	−33,5	−29,5
SL-C06		503	124	103	37	88	197	186	−40,8	−156	−33,1	−32,5
SL-C07		179	19	15	49	57	923	2186	−45,0	−270		
SL-C07 D		101	13	10	24	30	513	1147	−44,5			
SL-C09		681	192	124	51	94	126	52	−43.8	−158	−33,0	−32,8
SL-E01		37	5	3	0	2	0	0	−34,0			
Dl-D02		27	5	4	5	6	21	3	−31,8			
Dl-D05		37	8	6	2	5	64	135	−35,2			
Dl-E01		702	215	100	67	55	141	91	−41.5	−194	−32,9	−31,3
Dl-E03	4	271	70	40	15	22	40	45	−37,8	−179	−33,2	−30.5
HD-A05		4467	1940	1191	353	582	894	833	−54,4	−146	−37,8	−32,3
HD-A11 F		4028	2174	1332	287	537	426				−38,5	−33,5
HD-A13	4	3863	1918	1260	317	715	1000	3874	−56,0	−181	−40,0	−34,5
HD-B01		4668	2279	1475	487	834	1394	2987	−55,5	−204	−39,3	−34,2
HD-B09 F		4265	2296	1380	374	561	562	n.d.	−54,9	−235	−38,4	−32,7
HD-B11		4633	2199	1432	484	836	1286	1310	−56,1	−217	−39,3	−34,2

Tab. 2: cont.

Sample	Biostrati-graphy	C_1 (ppb)	C_2 (ppb)	C_3 (ppb)	iC_4 (ppb)	nC_4 (ppb)	C_5 (ppb)	C_6 (ppb)	$\delta^{13}C_1$ (o/oo)	δDC_1 (o/oo)	$\delta^{13}C_2$ (o/oo)	$\delta^{13}C_3$ (o/oo)
HD-C01		3998	2083	1283	345	611	1013	1453	−61,9	−200	−45,4	−37,9
HD-D01		4017	2596	1935	613	1116	2226	9195	−53,1	−192		
HD-E01	4	990	392	246	162	215	479	2867	−51,0	−215	−38,4	−33,8
HD-E09		917	390	258	82	154	272	303	−51,0	−150		
BE-A07 F		3445	1529	51	185	333	254		−53,4	−222	−35,7	−31,0
BE-A09		4197	1663	1030	269	583	686	431	−54,6	−215	−37,0	−32,2
BE-A11	4	3651	1532	902	231	512	643	478	−53,7	−194	−36,8	−31,8
BE-B09 F		13360	6690	420	509	738	529		−62,6	−262	−41,6	−33,7
BE-B12		13803	6526	2815	694	1220	1535	1176	−63,5	−260	−42,9	−35,2
BE-C07	3	8609	3763	1765	482	882	1141	1009	−61,5	−249	−43,1	−35,8
PL-A05		23763	7832	2560	650	997	1191	1165	−66.3	−219	−36,1	−29,9
PL-B04 F		32210	11269	3700	730	1197	834		−60,6	−221	−30.8	−27.2
PL-B06	1	25916	9652	4052	690	1559	1082	497	−60,6	−222	−32.5	−28.6
PL-C07	1	21233	6857	3000	849	1466	2017	2380	−58,0	−241	−31,0	−27,3
PL-D09		14449	4950	2303	673	1156	1428	1911	−57.9	−223	−32,1	−27,5
PL-E06 F		19976	6876	2940	782	1040	777		−62,7	−233	−33,6	−28.6
PL-E08 F		23934	7013	2737	804	1331	1598	1229	−61,5	−221	−34,8	−30,1
PL-F09 F		10598	3124	1158	294	441	400		−51,4	−202	−31,9	−28,2
PL-F10	3	11771	2834	1213	335	629	849	703	−52,6	−214	−32,7	−29,0

1: Posidonia shale
2: Basal U. Toarcian
3: U. Toarcian
4: U. Toarcian-L. Aalenian

D: duplicate sample preparation and measurements
F: sample preparation and measurements by an independent laboratory